



Europäisches Patentamt
European Patent Office
Office européen des brevets

(1) Publication number:

0 287 224
A2



EUROPEAN PATENT APPLICATION

(2) Application number: 88302535.5

(3) Int. Cl.: B01D 53/34

(2) Date of filing: 23.03.88

(4) Priority: 16.04.87 US 39324
15.07.87 US 73980

(4) Date of publication of application:
19.10.88 Bulletin 88/42

(4) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(7) Applicant: ENERGY AND ENVIRONMENTAL
RESEARCH CORPORATION
18 Mason
Irvine California 92714(US)

(7) Inventor: Heap, Michael P.
518 Carnation
Corona Del Mar, California 92625(US)
Inventor: McCarthy, James M.
438 1/2 Holly Street
Laguna Beach, California 92651(US)
Inventor: Chen, Shih L.
34 Fort Sumter
Irvine, California 92720(US)
Inventor: Pershing, David W.
1582 Tomahawk Drive
Salt Lake City, Utah 84103(US)

(7) Representative: Orr, William McLean et al
URQUHART-DYKES & LORD 6th Floor, Tower
House Merrion Way
Leeds West Yorkshire, LS2 8PA(GB)

(5) Methods of removing NO_x and SO_x emissions from combustion systems using nitrogenous
compounds.

(5) The present invention relates to methods for selectively reducing NO_x so that nitrogen can be removed from emission effluent streams and NO_x emissions can be reduced to very low levels. In addition, the present invention teaches a method whereby NO_x and SO_x may be simultaneously removed from the effluent stream.

The present invention teaches the reduction of NO_x with -NH and -CN containing selective reducing agents such as ammonium sulfate, urea, NH₃, and cyanuric acid. Initially, the selective reducing agent is decomposed in a fuel-rich environment to form highly reactive decomposition products. The reaction of the selective reducing agent to produce its decomposition products, such as NH, NH₂, isocyanic acid, and related reaction intermediates, takes place in an oxygen-free, fuel-rich decomposition zone with the reaction temperature in the range of from about 300°F (150°C) to about 3000°F (1650°C).

After the selective reducing agent is decomposed in the absence of oxygen, the decomposition products are contacted with the effluent stream containing NO_x. At this point the oxygen level of the stream must be carefully controlled to provide an excess of oxygen so that the selective reduction of the NO_x species will occur. It may be necessary at this point to inject air into the effluent stream in order to maintain the proper oxygen-rich (fuel-lean) conditions for NO_x reduction. In this second "reaction zone," NO_x reduction takes place at temperatures of from approximately 500°F (280°C) to approximately 2800°F (1425°C).

The present invention can also be used in conjunction with SO_x control technology. Specifically, species used to control SO_x, such as limestone, dolomite, quicklime, and hydrated lime, can be added in conjunction

A2
EP 0 287 224
EP

0 287 224

with the selective reducing agent for simultaneous NO_x and SO_x control.

METHODS OF REMOVING NO_x AND SO_x EMISSIONS FROM COMBUSTION SYSTEMS USING NITROGENOUS COMPOUNDS

BACKGROUND

The Field of the Invention

5 The present invention is related to methods for reducing nitrogen oxide ("NO_x") emissions from pollution sources, such as combustion systems. More particularly, the present invention relates to the noncatalytic, selective reduction of NO_x by -NH and -CN containing compounds to achieve very low levels of NO_x emissions.

10

The Background of the Invention

15 One of the major problems in industrialized society is the production of air pollution from numerous sources. Air pollution can take various forms. Some of the different types of air pollutants include particulate emissions such as coal ash, partially burned coal particles, and the like, sulfur compounds such as SO₂ and SO₃ (sometimes collectively referred to as "SO_x"), ozone, carbon oxide emissions, volatile hydrocarbon emissions, and emissions of nitrogen oxides (commonly referred to collectively as "NO_x"). Pollution sources include automobiles, industrial plants, small commercial establishments, such as dry cleaners and service stations, and even nature itself.

20 Combustion effluents and waste products from particular types of sources have proven to be major contributors to damaging air pollution when the effluents are discharged into the atmosphere. Unless these waste products are treated before their release into the atmosphere, serious smog and air pollution problems are encountered.

25 It will be appreciated that high concentrations of air pollutants have serious deleterious impacts on the health and general welfare of society. Air pollution is known to aggravate certain medical conditions (such as heart and lung problems) and is known to cause problems in the environment, ranging from corrosion to acid rain.

30 One of the most common components found in polluted air is nitrogen dioxide ("NO₂") which is known to be toxic. Nitrogen dioxide, which is brown in color, undergoes a series of reactions, known generally as "photochemical smog formation," in the presence of sunlight and airborne hydrocarbons. These reactions result in a marked decline in overall air quality.

35 While NO₂ is produced from a wide variety of pollution sources, its primary source is from nitric oxide ("NO") released into the air. NO is commonly formed during combustion processes, including internal combustion engines in automobiles, hydrocarbon fuel power plants, process furnaces, incinerators, coal-fired utility boilers, glass furnaces, cement kilns, oil field steam generators, gas turbines, and other similar installations.

40 There are two primary mechanisms for the formation of nitrogen oxides in the combustion processes. Within the high temperature portions of a flame, atmospheric oxygen can react with molecular nitrogen ("N₂") to form NO by the high temperature "thermal fixation" mechanism.

45 In addition, fuels which contain large amounts of nitrogen chemically bound within the fuel structure may produce significant NO_x emissions as a result of the oxidation of the fuel nitrogen during the burning process. This source of NO_x emission (often termed "fuel NO_x") is the predominant source of NO_x with the combustion of coal, heavy oils, biological and agricultural residues, and some municipal, industrial, and agricultural wastes.

50 Since NO is the only oxide of nitrogen which is stable at the high temperatures encountered in these types of combustion processes, NO is the predominant nitrogen emission product. At normal atmospheric temperatures, however, the equilibrium between NO and NO₂ favors NO₂. Hence, NO formed by combustion is generally discharged into the atmosphere as NO, and only subsequently converted to NO₂. In order to control NO₂ emissions, therefore, it is necessary to eliminate NO before it enters the atmosphere.

55 There have been considerable efforts in the art to find effective ways to remove oxides of nitrogen from waste gases so that these waste gases may be discharged to the atmosphere without harm to the environment.

Because the "thermal fixation" of atmospheric nitrogen is exclusively a high temperature phenomenon,

occurring above 2800°F (1540°C), it has been possible to achieve significant reductions in NO_x emissions from the combustion of nitrogen-free fuels (such as natural gas or gasoline) by reducing the overall temperature in the combustion zone. This is accomplished using techniques such as exhaust gas recirculation in automobiles or flue gas recirculation in utility boilers.

5 Fuel NO_x formation is most easily controlled by limiting the amount of oxygen present during the period in which the nitrogen species are being evolved from the fuel matrix. Techniques such as a staged combustion, overfire air addition, and "burners out of service" all use this concept to limit fuel and nitrogen oxidation.

More recently, it has been recognized that limited amounts of hydrocarbon fuels, particularly those
10 which do not contain fuel nitrogen, can be used to effectively incinerate NO formed in the main combustion zone by creating a fuel rich (oxygen deficient) environment downstream of the primary combustion zone. This technique is generically termed "reburning," and like the other combustion modification techniques, is capable of producing overall NO_x reductions in excess of 50% under optimized conditions.

Unfortunately, at the present time, none of the combustion modification techniques are capable of
15 producing very high levels of NO_x control in the range of approximately 80% to 90%. To achieve extremely low NO_x emission levels, it is necessary to utilize some type of downstream, effluent gas cleanup system.

It has been found in the art that removal of NO₂ from a combustion effluent stream is relatively easy since it reacts with water and air to form nitric acid. NO₂, therefore, is commonly removed by aqueous scrubbing. If a base, such as ammonia, is added to the scrub water, the nitrogen scrubbing process is
20 facilitated and ammonium nitrate is produced. If limited amounts of NO are present along with the NO₂, the NO may be coscrubbed, thereby yielding ammonium nitrate.

Most chemical scrubbing techniques are subject to the limitation that they are only effective for mixtures of nitrogen oxides which are predominantly NO₂, rather than predominantly NO. This presents a problem because NO is the predominant species at the high temperatures generally encountered in flue
25 gases. As a result, various processes have been developed in the art for oxidizing NO to NO₂ so that the relatively inexpensive and convenient scrubbing processes may take place.

Several processes known in the prior art involve contacting the gaseous flow which includes NO, with various organic compounds (such as aldehydes, alcohols, ketones, organic acids, and the like) in the presence of oxygen. By such processes, the NO is oxidized to NO₂ which can then be removed by
30 scrubbing as described above. None of these processes, however, are capable of efficiently producing very low levels of NO_x emissions.

An alternative approach for removing NO from flue gases and other streams of pollutants is to reduce NO to nitrogen and water, which may then be discharged to the atmosphere. Reduction of NO_x may be accomplished with or without catalytic assistance. Practically, the noncatalytic processes are preferable
35 because they are not subject to the usual disadvantages of employing catalysts. Some of these additional disadvantages include higher expense associated with the catalyst, the potential of catalyst plugging, the expense and difficulty of contacting the combustion effluents with the catalyst, and the danger that the catalyst will disintegrate and be emitted into the atmosphere.

Alternatively, NO_x reduction processes often teach the removal of NO_x from flue gases by reduction of
40 the NO by the addition of ammonia, urea, or ammonia precursors, alone or in combination with some other combustional material, while the waste gas is at a relatively high temperature (generally from about 700°C to about 1200°C).

An example of such an NO reduction process is described in United States Patent No. 3,900,554 to Lyon, issued August 19, 1975, entitled "Method for the Reduction of the Concentration of NO in
45 Combustion Effluents Using Ammonia." The process disclosed in that patent teaches the reduction of NO to N₂ by injecting ammonia under excess oxygen conditions into the combustion effluent stream at a temperature from about 870°C to about 1100°C. If the ammonia is injected along with a second reducing agent, such as hydrogen, NO will be reduced at temperatures as low as 700°C.

A corresponding NO reduction process is described in U.S. Patent No. 4,335,084 to Brogan, issued
50 June 15, 1982, entitled "Method for Reducing NO_x Emissions from Combustion Processes." The process disclosed in that patent is somewhat analogous to that disclosed by Lyon in that NO is reduced by a selective, noncatalytic, reaction with ammonia; however, according to the Brogan process, the reaction occurs under fuel-rich conditions and the reaction temperature window is considerably higher (1800-3000°F; 1040-1650°C).

55 Recent data indicate that similar results can be achieved under both fuel-rich and fuel-lean conditions with urea injection. In U.S. Patent No. 4,208,386 to Arand, et al., issued June 17, 1980, entitled "Urea Reduction of NO_x and Combustion of Effluents," a method for selectively reducing NO_x in combustion effluents containing at least 0.1 volume percent oxygen at temperatures in excess of 1300°F (700°C) is

described. As with the Lyon invention for ammonia, the optimum temperature window for urea injection under excess air conditions is relatively low (1300-2000°F; 700-1100°C).

In a subsequent U.S. Patent No. 4,325,924, again to Arand, et al., issued April 20, 1982, entitled "Urea Reduction of NO_x in Fuel Rich Combustion Effluents," the authors disclose the existence of a high-temperature window (1900-3000°F; 1040-1650°C) where urea can also be used to selectively reduce NO_x emissions under fuel-rich conditions.

The above-referenced material demonstrates that while NO_x emissions can be selectively reduced by ammonia, ammonia producing compounds and urea, the optimum temperature appears to depend primarily on whether selective reduction reactions are being conducted under fuel-rich (high temperatures required: 1900-3000°F; 1040-1650°C) or fuel-lean conditions (moderate temperatures: 1300-2000°F; 700-1100°C). However, none of the above references discloses a process for achieving very low concentrations of NO_x emissions.

One investigator has suggested that cyanuric acid could possibly serve as a species for reducing NO_x. Perry, et al., "Rapid Reduction of Nitrogen Oxides in Exhaust Gas Streams," Nature pp. 857-858 (December 1988) (hereinafter "Perry Process"). Perry states that NO_x can be reduced by using isocyanuric acid (produced by decomposing cyanuric acid) at temperatures above 600°C (1100°F). Perry further reports "the absence of the need for controlled amounts of oxygen." While that process reportedly showed some possible benefits for use in reducing the level of NO_x emission in the laboratory setting, the reported results have not been duplicated in actual combustion application.

It is presently believed that two primary factors account for the discrepancy between the results achieved by the Perry Process and those results obtained in actual application. Perry conducted the "flow tube reactor" experiments in an inert atmosphere. When typical other combustion species such as CO₂, CO, and water are present in the reaction atmosphere, however, the beneficial reduction of NO_x by cyanuric acid is markedly changed, especially with respect to the optimum temperature and the influence of oxygen.

Similarly, it is believed that by conducting experiments in the presence of stainless steel, Perry produced drastically different results than those achieved with no stainless steel present. It is presently believed that the stainless steel acted as a catalyst of the reaction. As a result, while the use of cyanuric acid provided some hope for obtaining low levels of NO_x emission at moderate temperatures (600°C to 1100°C), in actual combustion application, the reduction of NO_x by cyanuric acid has been found to be ineffective at moderate temperatures, and at best, no more effective than existing techniques, at high temperatures.

Another group of pollutants which are of major importance are the sulfur oxides (generally collectively designated "SO_x"). Sulfur oxides are primarily emitted in the form of sulfur dioxide ("SO₂"), with small amounts of accompanying sulfur trioxide ("SO₃"). Since there is no harmless gas phase sulfur species analogous to N₂, combustion modification has not been useful for controlling SO_x emissions. Exhaust gas cleanup systems, however, including both wet scrubbing and spray drying techniques, are well known and effective.

High temperature (1800°F to 2800°F; 980-1540°C) injection of dry, pulverized limestone has also been used to reduce sulfur emissions. In addition, several recent investigations have shown that hydrated lime (Ca(OH)₂) is effective in reducing SO_x emissions. None of the current literature, however, shows that dry sorbent injection can be directly combined with reducing agent injection to achieve optimum NO_x and SO_x control simultaneously and with relatively small capital cost. Such a process would be a major advancement in the art.

From the discussion above, it is apparent that what is currently needed in the art are methods for the selective, noncatalytic reduction of NO_x which produce NO_x emissions well below those obtainable using prior art methods. It would be an advancement in the art to provide such methods which employed a process which effectively produced emission levels below 100 ppm without a catalyst and using inexpensive and readily available reactants. It would be a further advancement in the art to provide methods for simultaneously controlling NO_x and SO_x emissions.

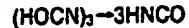
Such methods are disclosed and claimed below.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The present invention relates to methods for selectively reducing NO_x so that nitrogen oxides can be removed from emission effluent streams and NO_x emissions can be reduced to very low levels. In addition, the present invention teaches a method whereby NO_x and SO_x may be simultaneously removed from the effluent stream.

The present invention teaches the reduction of NO_x with NH₃, urea, cyanuric acid, and related compounds. Contrary to the teachings of the existing literature, however, the present invention teaches a two-step reaction process under carefully controlled conditions for reducing NO_x to very low levels.

Initially, the selective reducing agent (such as ammonium sulfate, urea, or cyanuric acid) is decomposed. It is presently believed that this decomposition forms NH₂ radicals. This reaction takes place in an oxygen-free, fuel-rich "decomposition zone." For example, when cyanuric acid is decomposed, it is most likely to form isocyanic acid. The general mechanism for producing isocyanic acid from cyanuric acid is as follows:



It is presently preferred that the reaction temperature in this decomposition zone be maintained in the range of from about 300°F (150°C) to about 3000°F (1650°C), and preferably in the range of from about 1200°F (650°C) to about 1900°F (1040°C) when NH₃, urea, or a related compound is the reducing agent, and preferably in the range of from about 1400°F (750°C) to about 2400°F (1300°C) when cyanuric acid is the reducing agent.

It will be appreciated, furthermore, that NO_x may or may not be a part of the oxygen deficient gases in the oxygen-free, fuel-rich decomposition zone. That is, the production of the reaction intermediates in the oxygen-free decomposition zone may take place within the combustion area ("combustion zone") which produces the effluents. Alternatively, reducing agent decomposition may occur at a location remote from the combustion zone in the presence of CO and water. If the second alternative is chosen, the reducing agent decomposition species will then be injected into the effluent stream at an appropriate location.

After the reducing agent is decomposed in the absence of oxygen, the decomposition stream is mixed with the effluent stream containing NO_x. At this point, the oxygen level of the stream must be carefully controlled to provide an excess of oxygen. It may be necessary at this point to inject air into the effluent stream in order to maintain the proper conditions for NO_x reduction.

In this reaction zone, NO_x reduction takes place at temperatures in the range of from approximately 500°F (250°C) to approximately 2800°F (1425°C). The selective reduction of NO_x in this zone is relatively fast; but residence times in excess of at least 30 milliseconds are preferred in order to assure that complete micromixing occurs.

The molar ratio of equivalent nitrogen (moles of nitrogen) in the reducing agent to nitrogen in NO_x to be removed should be approximately 0.5:1 to approximately 10:1. Increasing the ratio of the reducing agent to the NO_x increases the extent of NO_x reaction; however, it may also increase the overall cost of the control technology and the probability of undesirable trace species produced by the reaction of the reducing agent being emitted.

The present invention can also be combined with SO_x control technology. Specifically, species used to control SO_x (such as limestone, dolomite, quicklime, and hydrated lime) can be added to the NO_x reducing agent for injection into the effluent stream. Thus, simultaneous NO_x and SO_x control can be achieved.

It is, therefore, a primary object of the present invention to provide methods for reducing NO_x emissions which are highly selective, noncatalytic, and which are capable of providing overall emission reductions in excess of 90% using a relatively low cost process.

It is a related object of the present invention to provide such methods which are capable of producing exhaust NO_x emission levels at acceptably low levels which are significantly lower than those achieved under typical combustion conditions.

It is another object of the present invention to provide methods which are capable of simultaneously reducing emissions of both NO_x and SO_x.

It is also an object of the present invention to provide methods for using cyanuric acid for reducing NO_x which are effective in the actual combustion environment.

These and other objects of the invention will become apparent upon reading the following detailed description and appended claims, and upon reference to the appended drawings.

50 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph which illustrates the direct application of ammonia, urea, and related compounds according to the teachings of the existing literature under fuel-lean conditions.

Figure 2 is a graph which illustrates the selective reduction of NO_x emissions with NH₃ injection under the mechanisms taught by Lyon (solid squares), and Brogan (solid diamonds) as compared to the 2-zone method of the present invention (open circles).

Figure 3 is a graph which illustrates the direct application of cyanuric acid injected according to the teachings of the existing literature under both fuel-rich and fuel-lean conditions.

Figure 4 is a graph which illustrates the reduction of NO_x emissions under the mechanism taught by Perry and under both laboratory and actual conditions.

5 Figure 5 is a graph which illustrates the reduction of NO_x emissions using the same amount of cyanuric acid as illustrated in Figure 1, but using the two-zone method of the present invention.

Figure 6 is a graph which illustrates the selective reduction of NO_x emissions using urea injection under the mechanism taught by Arand et al. (solid symbols) under both fuel-rich and fuel-lean conditions compared to the 2-zone method of the present invention (open symbols).

10 Figure 7 is a graph which summarizes the influence of various NH and CN compounds on NO_x emissions and CO emissions using the 2-zone method of the present invention.

Figure 8 is a graph which illustrates the influence of the decomposition zone stoichiometry.

Figure 9 is a graph which illustrates the influence of the reduction zone stoichiometry.

15 Figure 10 is a graph which illustrates the SO_x reduction which can be achieved using a cyanuric acid/CaO slurry.

Figure 11 is a graph which illustrates the SO₂ capture which can be achieved with the CaO-slurry of this invention relative to the capture achieved with hydrated limes and raw CaO.

20 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

I. General Discussion

The present invention is related to a two-stage reaction method for reducing NO_x within an effluent stream using -NH or -CN decomposition products. The effluent stream may originate with a fixed facility such as a boiler, refinery heater, industrial furnace, gas turbine, municipal waste incinerator, or internal combustion engine, or with a mobile source such as a gasoline or diesel engine in a motor vehicle.

25 The present invention provides an extremely effective method of eliminating NO_x pollutants. NO_x pollutants can be reduced by more than approximately 90 percent, thereby producing exhaust NO_x emission levels, under typical conditions, significantly below 100 ppm.

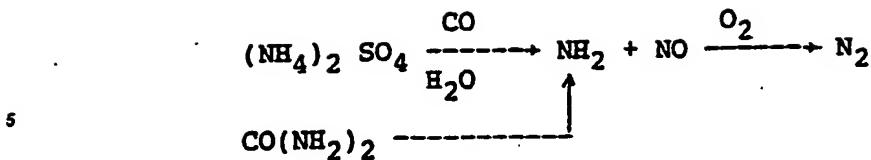
30 As mentioned above, the present invention operates by the use of an amine, or cyano containing selective reducing agent such as ammonium sulfate, urea, melamine, or cyanuric acid. Other potentially useful compounds include such species as ammonium carbonate, ammonium bicarbonate, ammonium formate, ammonium oxalate, ammonia, biuret, triuret, NH₂CN, Ca(CN)₂, CaCN₂, NaOCN, and dicyanodiamide.

35 Under the methods now known in the art, urea, ammonia, and ammonia salts are known to be useful as NO_x reducing agents at temperatures between 1300 and 2000°F (700 and 1100°C) for fuel-lean injection and at temperatures from 1900 to 3000°F (1040 to 1650°C) for fuel-rich injection. However, the existing art does not teach that reductions can be achieved with low temperature, fuel-rich injection and it is incapable 40 of producing emission levels significantly below 100 ppm. Indeed, current commercial practice is to employ selective high cost catalytic reduction processes when extremely low emission levels are required. The present invention overcomes the obstacles previously encountered when applying the prior art to actual practice.

45 As mentioned above, the present invention also operates by the use of cyanuric acid as an NO_x reducing agent. Under the methods now known in the art, cyanuric acid is not useful as an NO_x reducing agent under conditions typical of actual practice without the use of a stainless steel catalyst. The present invention overcomes the obstacles previously encountered in applying the Perry cyanuric acid process in actual practice.

In the first reaction zone of the present invention, the selective reducing agent is decomposed. As 50 mentioned above, this reaction zone can be referred to generally as the "decomposition zone" and may be within the combustion zone which produces the NO_x emissions, or it may be separate. Decomposition of the selective reducing agent is necessary in order to provide appropriate species which are effective for NO_x reduction.

It is presently believed that the selective reducing agent proceeds by the following general reactions:



While the details of the decomposition process have not been fully characterized at the present time, it appears likely that NH and NH₂ are key intermediate species. It is presently believed that cyanuric acid decomposition proceeds by the following general reaction:



That is, cyanuric acid is decomposed to isocyanic acid in the presence of heat. It is possible that isocyanic acid intermediates or other products may participate in the result achieved by the present invention. For clarity of discussion, the reaction mechanisms shown above are discussed; however, these proposed mechanisms are not intended to limit the scope of the present invention.

The decomposition of the reducing agent must take place in a fuel-rich environment; thus, the decomposition can take place within the combustion effluent stream at a point where oxygen is deficient and the primary gas phase species are CO, CO₂, N₂, and H₂O. In the alternative, the decomposition of the reducing agent may take place in a separate, oxygen-free decomposition zone, probably containing CO and H₂O, but apart from the NO_x containing effluent stream. The reducing agent may be injected in any of a number of forms. For example, a dry solid powder, an aqueous solution, a slurry, or an alcoholic solution have all been found to be acceptable.

The decomposition must take place at somewhat elevated temperatures. It is presently preferred that the decomposition take place at temperatures between approximately 300°F (150°C) and approximately 3000°F (1650°C). More specifically, it is presently preferred that the decomposition of reducing agent take place at temperatures from about 1200°F (650°C) to about 1900°F (1040°C) when NH₃, urea, or a related compound is the reducing agent, and preferably in the range of from about 1400°F (750°C) to about 2400°F (1300°C) when cyanuric acid is the reducing agent. Indeed, for some applications when cyanuric acid is used, temperatures between about 1400°F (750°C) to about 1800°F (980°C) are found to be most effective.

The time which the reducing agent spends within the decomposition zone should be sufficient to allow at least partial decomposition of the reducing agent species. The reaction time within this zone is preferably from approximately 0.005 seconds to approximately 5.0 seconds. More preferably, the time within the decomposition zone is from approximately 0.03 seconds to approximately 2.0 seconds.

Once the reducing agent is decomposed it may be introduced into the effluent stream in order to accomplish complete reduction of the NO_x species within the stream. This second reaction zone must be at a location in the effluent stream which is oxygen rich.

For example, the reduction of NO_x by the decomposed cyanuric acid species is believed to take place by the following global mechanism: HNCO + NO → N₂ + CO₂ + H₂O

The temperature within the reaction zone is preferably maintained between approximately 500°F (250°C) and approximately 2600°F (1425°C). More preferably the temperature within the reaction zone should be maintained within the range of approximately 800°F (425°C) to approximately 2400°F (1300°C).

The selective reduction of NO_x by the decomposition product species occurs at a relatively fast pace. In order to assure complete reaction of the species, however, residence times from approximately 30 milliseconds to approximately 5.0 seconds are required. More preferably reaction times within the range of approximately 100 milliseconds to approximately 2.0 seconds are required.

It will be appreciated that under certain circumstances it may be desirable to enhance the effectiveness of the reaction zone by the addition of one or more reaction enhancers. These may include, for example, radical generating promoters such as hydrogen, methanol, natural gas, propane, carbon monoxide, and light petroleum fuels. The additional species may also include catalysts such as stainless steel, palladium, platinum, tungsten, nickel, cobalt, gold, silver, and manganese.

It is presently preferred that the molar ratio of equivalent nitrogen ("moles of N") in the reducing agent to the moles of N in the NO_x to be removed should be in the range of from 0.5:1 to about 10:1. More specifically, the range of from about 0.7:1 to about 3:1 is preferred. Increasing the ratio of reducing agent to the NO_x increases the extent of NO_x reduction; however, it also increases the overall cost of the control technology, as well as the probability of additional undesired species being emitted.

It is also presently preferred that the air/fuel stoichiometric ratio within the decomposition zone be

maintained within certain ranges. Air/fuel ratios within the range of about 0.7 to 1.0 are found acceptable, with the most preferred range being from about 0.9 to about 1.0.

In addition to providing NO_x reduction, the present invention can also be used in conjunction with SO_x control. As was mentioned above, injection of dry, pulverized limestone at temperatures from approximately 5 1800°F (980°C) to approximately 2800°F (1540°C) can be used to reduce sulfur emissions. In addition, hydrated lime (" $\text{Ca}(\text{OH})_2$ ") is more effective than either the raw limestone or intermediate reactant CaO.

Thus, it is within the scope of the present invention to inject a dry sorbent (such as hydrated lime), in conjunction with the injection of the NO_x reducing agent or its decomposition products. Therefore, sulfur reduction technology can easily be combined with the present invention in order to simultaneously reduce 10 NO_x and SO_x emissions.

II. Experimental Results

15 As noted briefly above, the existing literature reports that ammonia, ammonia salts, and urea can be used to reduce NO_x emissions under excess air conditions at moderate temperatures. Figure 1 is a graphical representation of data obtained using the process described by Lyon for NH_3 and by Arand, et al. for urea.

The data set forth in Figure 1 were obtained in a six-inch diameter refractory lined furnace where the 20 primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU/hour. The gas phase NO concentration prior to the injection of the reducing agent (" NO_x ") was 240 ppm. Ammonia was added in the form of a pure gas; the other compounds were added in the form of a dry powder mixed with an inert, limestone, to facilitate feeding. In each instance the nitrogen in the reducing agent was 1.5 times the molar nitrogen present as NO.

25 The data are presented with the vertical axis showing the ratio of final NO (" $(\text{NO})_f$ ") to initial NO (" $(\text{NO})_i$ "). The horizontal axis represents injection temperature of the nitrogen reducing agent into the refractory-lined furnace.

The data shown on Figure 1 indicate that NO_x reductions can be achieved using the process described by Lyon and Arand et al. Because this furnace is not an isothermal reactor, but rather the temperature is 30 falling at approximately 700°F/second (370°C/second), the actual reaction temperature is always slightly lower than the apparent temperature at the point of injection. Thus, an optimum injection temperature of approximately 2100°F (1150°C) corresponds to an actual reaction temperature of 1800°F (980°C) to 1900°F (1040°C).

With further reference to Figure 1, a stoichiometric ratio ("SR") of 1.25 existed and indicates that 25% 35 excess oxygen was present in the flue gas. Significant NO reductions were achieved with all of the compounds tested and the dependence with respect to temperature was similar for urea and the ammonia compounds. The best performance was achieved with ammonia and ammonium salts.

Figure 2 illustrates results obtained with the two zone concept of this invention relative to ammonia injection using the existing art. In the two-zone experiments, the NH_3 was injected at 1900°F (1040°C) and 40 the temperature of the secondary air addition point was progressively decreased. These results clearly indicate that there exists a third regime not disclosed in the previous art where NH_3 can be injected under fuel-rich conditions and caused to decompose to produce intermediate species which are more effective than those produced by direct injection at higher temperatures under either fuel-rich or fuel-lean conditions.

Figure 3 shows the results of an analogous set of experiments to those shown in Figure 2. Again these 45 experiments use the 50,000 BTU/hr. refractory-lined furnace but with urea injection. The solid symbols indicate the existing art with high temperature urea injection under fuel-rich conditions and medium temperature urea injection under fuel-lean conditions as described by Arand, et al.

As discussed briefly above, the Perry, et al., article reports that cyanuric acid can be used to reduce NO_x , supposedly without the need for controlled amounts of oxygen. Figure 3 is a graphical representation 50 of data obtained using the process described by Perry et al. under combustion conditions. The data set forth in Figure 3 were obtained in a 6-inch diameter refractory-lined furnace where the primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU/hour. The gas phase NO concentration prior to cyanuric acid injection (" $(\text{NO})_i$ ") was 600 ppm. The cyanuric acid was added in the form of a dry powder mixed with an inert limestone to facilitate feeding.

55 The data is presented with the vertical axis showing the ratio of final NO ($(\text{NO})_f$) to initial NO ($(\text{NO})_i$). The horizontal axis represents injection temperature of cyanuric acid into the refractory lined furnace.

The data shown on Figure 3 indicates that NO_x reductions can be achieved using the process of Perry et al., irrespective of oxygen concentrations at temperatures much higher than those reported by Perry.

With further reference to Figure 3, a stoichiometric ratio of 1.25 indicates that 25% excess oxygen was present in the flue gas. NO reductions were achieved under both fuel-rich ($SR = 0.95$) and fuel-lean ($SR = 1.25$) conditions. As would be expected from the existing literature, the optimum temperature is lower in the case of fuel-lean injection than with fuel-rich injection. In these experiments the stoichiometry remained constant throughout the reactor. The temperature of the cyanuric acid injection was varied by changing the location of the injection point.

While these results show that significant NO_x reductions can be achieved using simple cyanuric acid injection, these results also suggest that (1) it is not possible to achieve extremely low NO_x emissions if the cyanuric acid reducing agent is decomposed and reacted under the same stoichiometric conditions and (2) the process does not work at all in actual combustion gases at the temperatures reported by Perry. These results are consistent with the poor performance which has been observed in practice.

Figure 4 shows results which were obtained in a flow reactor substantially similar to that used by Perry except that the composition of the reactor wall could be changed as required. These data help explain the apparent disagreement between the results shown in Figure 1 and those reported by Perry.

If cyanuric acid is injected at $650^{\circ}C$ into a stainless steel reactor containing only inert gases and NO, then significant NO reductions do indeed occur as reported by Perry (Bar 1). However, if the reactor has inert walls (e.g., quartz) or contains actual combustion products (e.g., CO, CO_2 , H_2O , etc.), the reduction is greatly reduced (Bars 2 and 3). Hence, the process reported by Perry will not be effective in a real boiler or engine environment because combustion products will inevitably be present and the bulk of the gas will never contact the walls of the reactor (which will likely not be stainless steel).

Figure 5 shows the results of an analogous set of experiments to those shown in Figure 3 using the two zone process of the present invention. The experiments which produced the data which are set forth in Figure 5 were conducted with the same facility and under the same experimental conditions as that shown in Figure 3. In particular, the same injection method is used, the same furnace was used, and the same natural gas firing rate was used. In both cases the nitrogen equivalent of the added cyanuric acid was 1.5 times the inlet NO.

In the experiments illustrated in Figure 5, the cyanuric acid was decomposed in an oxygen deficient zone prior to the reduction of NO_x . The overall stoichiometry in the oxygen deficient zone was 0.99 and the selective reaction was allowed to subsequently occur in a downstream zone with an overall stoichiometry of 1.02.

Again the temperature of the decomposition zone was varied by changing the location at which the cyanuric acid injection occurred. The temperature of the selective NO_x reduction zone was varied by changing the location at which the final air was added in order to make the overall stoichiometry fuel lean.

The data presented in Figure 5 demonstrate that remarkably higher NO_x reduction efficiencies can be achieved using the two zone process than that illustrated using the one zone process of Figure 3. In addition, a far broader window of acceptable performance exists in a process of the present invention as shown in Figure 5.

The results reported in Figure 5 indicate that optimum cyanuric acid decomposition zone temperatures are less than $2200^{\circ}F$, and the optimum selective NO_x reduction temperature is between approximately $1400^{\circ}F$ and approximately $1800^{\circ}F$ for the particular residence time and profile used in these experiments. The residence times used in these experiments were from about 0.01 seconds to about 1.0 seconds for the cyanuric acid decomposition zone and from about 0.01 seconds to about 2.0 seconds for the selective NO_x reduction zone.

Table 1 shows the results of detailed species measurements made within the two zones and in the exhaust. These data indicate that the two zone process does not produce significant quantities of ammonia ("NH₃") at any point in the process. This is probably because the likely key reactive intermediate is HNCO and not NH₃.

Table 1

<u>Species</u>	<u>Concentration at the end of the decomposition zone</u>	<u>Concentration at the end of the reaction zone</u>
HCN	1.0 ppm	0.3 ppm
NH ₃	3.0 ppm	< 0.1 ppm
HNO ₃	540 ppm	< 0.1 ppm

Figure 6 also shows data obtained with urea injection using the two zone concept of the present invention. The results using the present invention illustrate dramatically that significantly lower NO_x levels can be achieved using the two zone concept with controlled stoichiometry than with either the fuel-lean or fuel-rich injection of the schemes of the existing art. Again, a far broader temperature window of acceptable performance exists for the process of the present invention as shown in Figure 6.

The results shown in Figure 6 indicate that the optimum urea decomposition zone temperatures are less than 1900°F (1040°C) and the optimum selective NO_x reduction temperature is between approximately 1400°F (750°C) and approximately 1800°F (980°C) for the particular residence time, stoichiometry, and temperature profile used in these experiments. The residence times used in these experiments were from about 0.01 seconds to about 1.0 seconds for the urea decomposition zone and from about 0.1 seconds to about 2.0 seconds for the selective NO_x reaction zone.

Figure 7 summarizes the optimum results obtained with the two zone concept of the present invention. These data were again obtained in the six-inch diameter refractory-lined tunnel furnace with an initial NO concentration of 240 ppm. The selective reducing agent was injected at a rate to provide a molar equivalent nitrogen ratio of 1.5 times the inlet NO. The stoichiometry in the decomposition zone was maintained at 0.99 and the overall stoichiometry, after the addition of the final burn out air in the reaction zone was maintained at 1.02 for the two zone process (open bars). The shaded bars indicate the NO reduction achieved with fuel-lean injection according to the existing art.

Figures 8 and 9 summarize the results of companion experiments designed to characterize the influence of local oxygen concentrations in both the decomposition zone and the reaction zone. Figure 8 illustrates the dependence of the selective NO_x reduction zone on the stoichiometry in the cyanuric acid decomposition zone. These data suggest that the optimum environment for cyanuric acid decomposition is one deficient in oxygen where the primary gas phase species are CO₂, water, and nitrogen.

Figure 9 shows the impact of oxygen concentration in the selective NO_x reaction zone. These data confirm that it is critically important that the NO_x zone be operated with a slight excess of oxygen, and that further increases beyond approximately 0.5% oxygen only slightly degrade the performance of the overall process.

These data demonstrate that in the case of the solid materials (urea and ammonium sulfate), the NO reduction using the two zone process of this invention greatly exceeds that possible with the previous art under the conditions tested.

Figure 10 shows the results of testing using an NO_x control agent in conjunction with CaO in the slurry form. The data presented in Figure 10 clearly indicate that it is possible to achieve major reductions of both NO_x and SO_x emissions using the combined reagents of cyanuric acid and CaO. The reactivity of CaO with respect to SO₂ is particularly surprising in view of previously reported literature on CaO injection which states that poor SO₂ control is achieved with injection of commercial grade CaO (relative to injection of limestone or hydrated lime). The enhancement of performance appears to be directly related to the use of the slurry injection mechanism.

Figure 11 shows the results of testing using various SO₂ control concepts. The solid lines indicate typical performance by high and low efficiency atmospheric hydrates (Linwood and Colton respectively) and commercially produced lime (CaO). Figure 11 also shows data for a hydrate slurry (triangles) which resulted in essentially the same sulfur capture as was achieved with the hydrate alone. More importantly, however, Figure 11 illustrates data obtained with a quicklime slurry which indicate that very high capture levels can be achieved by simply slurring commercial CaO and injecting the slurry under normal conditions at approximately 2300°F (1250°C). These data suggest that it is not necessary to externally hydrate the sorbent and dry it; the performance of the quicklime slurry is equivalent to that of the best commercial

hydrate.

The experimental data presented above clearly indicate that using the two stage mechanism described above, very high levels of NO_x control can be achieved. At the same time, if the NO_x reducing agent is injected along with CaO or other sorbents, corresponding high levels of SO_x control can be achieved. As a result, the present invention provides a clear advancement in the control of NO_x and SO_x emissions.

III. Examples of Preferred Embodiments of the Present Invention

10 The following examples are given to illustrate the process of the present invention, but the examples are not intended to limit the scope of the present invention.

Example 1

15 In this example, a six-inch-diameter refractory-lined furnace was used and was fired by natural gas at a firing rate of 50,000 BTU/hour. The gas phase NO concentration prior to urea injection was about 240 ppm. Urea was injected into the furnace as a dry powder mixed with an inert substance (i.e., limestone) to facilitate handling.

20 The ratio of injected urea to NO in the combustion effluents was 1.5. The stoichiometric ratio within the furnace was approximately 1.25. That is, the furnace was operated so as to produce combustion effluents in which 25% excess O₂ was present. Urea was injected in the absence of O₂ at temperatures at about 2000°F (1100°C).

25 Under these conditions, about 40% reduction of NO was observed. This illustrates the fact that the injection of urea into combustion effluents in the presence of oxygen at moderate temperatures can produce some NO_x reduction as described in the existing art. Exhaust concentrations dramatically below 100 ppm are, however, not achieved under these conditions.

30 Example 2

In Example 2, the same facility as set forth in Example 1 was used. The nitrogen equivalent in the added urea was again 1.5 times the inlet NO which was 240 ppm.

35 In this example the urea was injected into an oxygen deficient zone with an overall stoichiometry of 0.99. The bulk gas temperature at the point of injection was about 2450°F (1340°C). The urea was allowed to selectively react with the NO during a residence time of approximately 300 milliseconds ("ms") after which additional air was added to bring the overall stoichiometry up to 1.02. The temperature at which the final burnout air was added was approximately 2250°F (1230°C).

40 Using these conditions, approximately 30% reduction of NO was observed. The final NO concentration was about 175 ppm. This illustrates the fact that injection of urea into a high temperature, fuel-rich zone can produce some selective reduction as described in the prior art, however, exhaust concentrations below 100 ppm are not achieved under these conditions.

45 Example 3

In this example the same facility as that set forth in Example 1 was used. The gas phase NO concentration prior to urea injection was about 240 ppm and the nitrogen equivalent in the added urea was about 1.5 times the inlet NO.

50 In this example the urea was decomposed in an oxygen deficient zone with an overall stoichiometry of 0.99. The reaction of the urea decomposition products and NO was allowed to occur subsequently in a downstream zone with an overall stoichiometry of 1.02. The temperature at the point of urea injection in the decomposition zone was approximately 1870°F (1020°C) and the temperature in the reaction zone after the addition of the final burnout air was about 1550°F (850°C).

55 Under these conditions about 80% reduction of NO was observed. Final NO concentration was about 45 ppm. This example demonstrates that the use of the two zone concept with low temperature injection into an oxygen deficient zone can produce remarkably higher reduction efficiencies than high temperature, fuel-rich injection (Example 2) or direct excess air injection (Example 1).

Example 4

In this example, a six-inch diameter refractory-lined furnace was used and was fired by natural gas at a firing rate of 50,000 BTU/hour. The gas phase NO concentration prior to cyanuric acid injection was about 600 ppm. Cyanuric acid was injected into the furnace as a dry powder mixed with an inert substance (e.g., limestone) to facilitate handling.

The ratio of injected cyanuric acid to NO in the combustion effluents was 1.5. The stoichiometric ratio within the furnace was approximately 0.95. That is, the furnace was operated so as to produce combustion effluents in which O₂ was deficient. Cyanuric acid was injected in the absence of O₂ at temperatures at about 1900°F (1040°C).

Using these conditions, little or no reduction of NO was observed. Final NO concentrations were in excess of 570 ppm. This illustrates the fact that injection of cyanuric acid into combustion effluents is not in itself an effective process for removing NO in the absence of stainless steel.

15

Example 5

In this example the same facility and reaction conditions as those set forth in Example 4 were used. The nitrogen equivalent of added cyanuric acid was about 1.5 times the inlet NO.

20 In this example cyanuric acid was decomposed in an oxygen deficient zone with an overall stoichiometry of 0.99. The reaction of the cyanuric acid decomposition products and NO was allowed to occur subsequently in a downstream zone with an overall stoichiometry of 1.01. The temperature of the decomposition zone was held at about 1900°F (1040°C) and the temperature in the reaction zone was about 1900°F (1040°C). The concentration of NO_x following the selective reaction zone was 115 ppm.

25 As in Example 3, this example demonstrates that remarkably higher reduction efficiencies can be achieved using the two-zone process of the present invention.

Example 6

30

In this example a flow reactor having stainless steel walls was employed. The nitrogen equivalent of added cyanuric acid was about 1.5 times the inlet NO. The only species in the reactor other than the NO and cyanuric acid reactants was argon. The initial concentration of NO was about 600 ppm and the reactor was maintained at a temperature of about 1200°F (650°C).

35 Under these conditions the final NO concentration was about 285 ppm. These results indicate that the process described generally by Perry is effective under idealized conditions.

Example 7

40

In this example the same conditions as those described in Example 6 were produced. The flow reactor, however, was equipped with quartz walls. Under these conditions the NO concentration was reduced from 600 ppm to about 565 ppm.

45 These results indicate that in the absence of stainless steel, the single step process described above is not effective in reducing NO emissions.

Example 8

50 Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU per hour. The gas phase NO concentration prior to cyanuric acid injection was about 600 ppm.

An initial fuel-rich, oxygen-free zone was maintained, the stoichiometric ratio being 0.99. The temperature in the first zone was maintained at approximately 1800°F (1040°C). Cyanuric acid was injected into 55 this zone in the form of a solid. Cyanuric acid was allowed to react in this zone for approximately 0.3 seconds.

Subsequently, air was added to the reactants to bring the stoichiometric ratio up to 1.02. The temperature within the oxygen-rich environment was maintained at approximately 1800°F (870°C). Mixing

between the cyanuric acid decomposition products and the combustion effluents in the second zone took place for approximately 0.5 seconds.

Under these conditions it was found that the concentration of NO_x was reduced from an initial concentration of about 600 ppm to a final concentration of about 30 ppm.

5

Example 9

Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU per hour. The gas phase NO concentration prior to cyanuric acid injection was about 600 ppm.

An initial oxygen-free zone was maintained, the stoichiometric ratio being 0.99. The temperature in the first zone was maintained at approximately 2500°F (1370°C). Cyanuric acid was injected into this zone in the form of a solid. Cyanuric acid was allowed to react in this zone for approximately 0.3 seconds.

15

Subsequently, air was added to the reactants to bring the stoichiometric ratio up to 1.02. The temperature within the oxygen-rich environment was maintained at approximately 2500°F (1370°C). Mixing between the cyanuric acid decomposition products and the combustion effluents in the second zone took place for approximately 0.5 seconds.

20

Under these conditions it was found that the concentration of NO_x was reduced from an initial concentration of about 600 ppm to a final concentration of about 360 ppm.

Example 10

25 Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU per hour. The gas phase NO concentration prior to cyanuric acid injection was about 600 ppm.

An initial oxygen-free zone was maintained, the stoichiometric ratio being 0.99. The temperature in the first zone was maintained at approximately 2200°F (1200°C). Cyanuric acid was injected into this zone in the form of a solid. Cyanuric acid was allowed to react in this zone for approximately 0.3 seconds.

30

Subsequently, air was added to the reactants to bring the stoichiometric ratio to about 1.28. The temperature within the oxygen-rich environment was maintained at approximately 1700°F (925°C). Mixing between the cyanuric acid decomposition products and the combustion effluents in the second zone took place for approximately 0.5 seconds.

35

Under these conditions it was found that the concentration of NO_x was reduced from an initial concentration of about 600 ppm to a final concentration of about 170 ppm.

Example 11

40

Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with Illinois coal at a firing rate of about 50,000 BTU per hour. The gas phase NO concentration prior to cyanuric acid injection was about 540 ppm.

An initial oxygen-free zone was maintained, the stoichiometric ratio being 0.90. The temperature in the first zone was maintained at approximately 2240°F (1225°C). Cyanuric acid was injected into this zone in the form of an aqueous solution. Cyanuric acid was allowed to react in this zone for approximately 50 milliseconds.

45

Subsequently, air was added to the reactants to bring the stoichiometric ratio up to 1.25. The temperature within the oxygen-rich environment was maintained at approximately 2000°F (1100°C). Mixing between the cyanuric acid decomposition products and the combustion effluents in the second zone took place for approximately 350 milliseconds.

Under these conditions it was found that the concentration of NO_x was reduced from an initial concentration of 540 ppm to a final concentration of 50 ppm.

55

Example 12

5 Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with sulfur containing natural gas at a firing rate of 50,000 BTU per hour. The gas phase SO₂ concentration prior to CaO injection was 4000 ppm.

The overall stoichiometric ratio being 1.25, the temperature at the point of injection was approximately 2200°F (1200°C). CaO was injected into this zone in the form of a slurry with the Ca/S ratio being 2.0. The reactants were allowed to react in this zone for approximately 400 milliseconds.

10 Under these conditions it was found that the concentration of SO₂ was reduced from an initial concentration of 4000 ppm to a final concentration of 1300 ppm.

Example 13

15 In this example the same facility and reaction conditions as set forth in Example 3 were used. In this example, however, ammonia gas was added instead of urea and the nitrogen equivalent in the ammonia was 1.5 times the inlet NO.

In this example the ammonia was decomposed in an oxygen deficient zone with an overall stoichiometry of 0.99. The reaction of the ammonia decomposition products and NO was allowed to occur subsequently in a downstream zone with an overall stoichiometry of 1.02. The temperature at the point of NH₃ injection and decomposition was held at about 1900°F (1040°C) and the temperature at the beginning of the reaction zone where the final burnout air was added was about 1550°F (850°C). The concentration of NO following the selective reaction zone was 120 ppm corresponding to a 50% overall reduction.

This example demonstrates that good NO_x reduction efficiencies can be achieved using ammonia gas 25 as a selective reducing agent with the two zone process of the present invention.

Example 14

30 In Example 14 the same facility and reaction conditions as set forth in Example 1 were used. Ammonium sulfate was added to provide the nitrogen equivalent of about 1.5 times the inlet NO.

In this example the ammonium sulfate was added under excess air conditions at a temperature of approximately 2100°F (1150°C). The overall stoichiometry was 1.25 corresponding to 25% excess O₂. The ammonium sulfate was allowed to decompose and selectively reduce the NO_x, both under excess oxygen 35 conditions. The concentration of NO_x following the reaction was about 95 ppm.

This example demonstrates that ammonium sulfate can be used to produce significant NO_x reduction under excess air conditions according to the existing art; however, the temperature window at which this occurs is extremely narrow. In this example increasing or decreasing the temperature by as little as 150°F (80°C) resulted in an emissions increase from 95 ppm to approximately 180 ppm.

40

Example 15

In Example 15, the same facility and reaction conditions as set forth in Example 3 were used. 45 Ammonium sulfate was added at a flow rate to provide the nitrogen equivalent of 1.5 times the inlet NO.

In this example the ammonium sulfate was decomposed in an oxygen deficient zone with an overall stoichiometry of 0.99. The reaction of the ammonium sulfate decomposition products and NO was allowed to occur subsequently in a downstream zone with an overall stoichiometry of 1.02. The temperature at the point of ammonium sulfate injection in the decomposition zone was held at about 1870°F (1020°C) and the 50 temperature at the beginning of the reaction zone where the final burnout air was added was about 1560°F (850°C).

Using these conditions about 85% reduction of NO was observed. The final NO concentration was about 34 ppm. This example demonstrates that extremely high reduction efficiencies can be achieved using the two zone process of this invention in conjunction with a solid -NH containing salt.

55

Example 16

In Example 16, the same facility and reaction conditions as set forth in Example 15 were used. Ammonium sulfate was added to provide a nitrogen equivalent of about 1.5 times the inlet NO.

- 6 In this example the ammonium sulfate was added to an oxygen deficient zone with an overall stoichiometry of 0.99. In this instance both the ammonium sulfate and the final burnout air (tertiary air) were added at a temperature of about 1850°F (1010°C). The final burnout air increased the overall stoichiometry to 1.02. The concentration of NO_x in the exhaust was 35 ppm corresponding an overall reduction of approximately 85%.
- 10 This example demonstrates that remarkable reduction efficiencies can be achieved using the two-zone process where the selective reducing agent is added into the fuel-rich zone simultaneously with the final burnout air.

Example 17

Data were obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone was fired with natural gas at a firing rate of 50,000 BTU/hr. The gas phase NO concentration in the primary zone was 80 ppm.

- 20 An initial, oxygen-free zone was maintained, the stoichiometric ratio being 0.90. Urea was injected into this initial, oxygen-free zone at a temperature of approximately 1870°F (1020°C). The urea was allowed to decompose in this zone for approximately 0.15 seconds.
- Subsequently, air containing NO was added to the stream from the decomposition zone. The NO concentration in the air stream was the equivalent of 160 ppm so that the total available NO was 240 ppm.
- 25 The temperature of the bulk gas at the point of air/NO injection was 1550°F (850°C).
- Under these conditions it was found that the concentration of NO_x in the exhaust was approximately 68 ppm. These results demonstrate that the selective reducing agent can be decomposed in a fuel-rich, moderate temperature decomposition zone fully separate from the NO_x to be reduced and then the decomposition products can be added to the stream containing the NO.

30

Example 18

Data were obtained using a six-inch-diameter refractory-lined furnace with a primary combustion zone fired with natural gas at a firing rate of 50,000 BTU/hour. The gas phase NO concentration prior to ammonium sulfate injection was 240 ppm. The nitrogen equivalent in the ammonium sulfate was 1.5 times the inlet NO.

- An initial oxygen-free zone was maintained, the stoichiometric ratio of this zone being 0.95. Ammonium sulfate was injected at approximately 1900°F (1040°C) as a dry solid and allowed to decompose.
- 40 Subsequently, air was added to the reactants to bring the stoichiometric ratio up to 1.05. The temperature at the air injection point was approximately 1600°F (870°C).
- Under these conditions it was found that the concentration of NO_x was reduced from an initial concentration of 240 ppm to a final concentration of 100 ppm. This example illustrates that significant reductions can be achieved using the two-zone concept of this invention at non-optimum stoichiometric ratios.

Example 19

- 50 Data were obtained using an eight-inch-diameter refractory-lined furnace where the primary combustion zone was fired with Illinois coal at a firing rate of 50,000 BTU/hour. Commercial quicklime (CaO) was injected as a dry powder at a flow rate to provide a Ca/SO₂ molar ratio equivalent to about 2.0. The dry quicklime was injected at approximately 2300°F (1250°C) and the overall stoichiometry was maintained at approximately 1.25.
- 65 Under these conditions it was found that the concentration of SO₂ in the exhaust was reduced by approximately 22%. These results show that relatively poor SO₂ capture efficiencies are achieved using commercial quicklime.

Example 20

5 Data were obtained using the same facility and reaction conditions as set forth in Example 19. In this instance a slurry prepared by mixing the commercial quicklime with water was injected at 2300°F (1250°C) with a calcium content equivalent to Ca/SO₂ ratio of 2.0.

Under these conditions it was found that the concentration of SO₂ in the exhaust was reduced by almost 60%. These data show that remarkably higher sulfur capture efficiencies can be achieved using commercial quicklime with slurry injection than with dry powder injection.

10

Example 21

15 Data are obtained using a six-inch-diameter refractory-lined furnace where the primary combustion zone is fired with natural gas at a firing rate of 50,000 BTU per hour. The gas phase NO concentration prior to cyanuric acid injection is 600 ppm and the SO₂ concentration is 4000 ppm.

An initial oxygen-free zone containing CO and H₂O is maintained, the stoichiometric ratio being 0.99. The temperature in the first zone is maintained at approximately 1900°F (1040°C). Cyanuric acid is injected into this zone in the form of a solid. Cyanuric acid is allowed to react in this zone for approximately 0.3 seconds.

20 Subsequently, the cyanuric acid decomposition products are added to a reaction zone having an excess of oxygen containing the NO_x to be reduced. In particular the stoichiometric ratio is 1.1. The temperature within the oxygen-rich environment is maintained at approximately 1800°F (870°C). Mixing between the cyanuric acid decomposition products and the combustion effluents in the second zone takes place for approximately 0.3 seconds.

25 In addition, a CaO slurry is injected into the reaction zone combustion products at 2200°F (1200°C).

Under these conditions it is found that the concentration of NO_x is reduced from an initial concentration of 600 ppm to a final concentration of 30 ppm and the SO₂ concentration is reduced from an initial concentration of 4000 ppm to 1300 ppm.

30

Example 22

35 Data are obtained using a 500 MW pulverized coal-fired boiler where the primary combustion zone is fired with a high sulfur midwestern bituminous coal. The primary zone in the lower furnace is fired under normal combustion conditions with excess oxygen corresponding to an overall stoichiometry of 1.05. Natural gas is injected above the primary combustion zone to reduce the overall stoichiometry to 0.97. Subsequently a CaO slurry containing calcium equivalent to a Ca/SO₂ ratio of 2.5 is injected at 2200°F (1200°C). Further downstream the final burnout air is added in the progressively staged manner. The initial air fraction includes an ammonium sulfate solution with a nitrogen content equivalent to 2.0 times the NO_x. This first 40 airstream is injected at 1850°F (1010°C) and is at the flow rate required to increase the overall stoichiometry to 1.02. Approximately 100 ms later the final remaining burnout air is added to raise the overall stoichiometry to 1.2.

45 Under these conditions it is found that the concentration of NO_x is reduced from an uncontrolled concentration of 550 ppm to a final concentration of 40 ppm. The SO₂ concentration is reduced from an initial concentration of 4000 ppm to 1500 ppm.

Example 23

50 Data are obtained using a large grate-fired incinerator which is charged with municipal solid waste at a rate of 1800 tons/day. The overall stoichiometry in the primary combustion zone corresponds to 1.5 (50% excess oxygen).

Ammonium sulfate is decomposed in a separate chamber by passing fuel-rich combustion products from a separate natural gas fired flame through a bed of ammonium sulfate. The temperature of this bed is 55 maintained at 1900°F (1040°C) and the nominal stoichiometry of the fuel-rich products is 0.99. The effluent from this decomposition zone is injected into the exhaust gas stream from the municipal waste incinerator

at a temperature of 1600°F (870°C). The equivalent nitrogen flow rate in the ammonium sulfate decomposition products is maintained at 3.0 times the NO_x flow from the incinerator.

Under these conditions it is found that the concentration of NO_x is reduced from an initial concentration of 900 ppm to a final concentration of 300 ppm.

5

Example 24

Data are obtained using a 350 cubic inch V8 engine where the engine is fueled with gasoline. The 10 engine is tuned such that the stoichiometry in the combustion zone is 0.98. The combustion products flow from the engine at approximately 900°F (480°C) and enter a decomposition zone where urea is being decomposed by contacting with the oxygen deficient combustion products.

Subsequently, final burnout air is added to produce a slight excess of oxygen corresponding to a stoichiometric ratio of 1.01. Under these conditions it is found that the concentration of NO_x is reduced from 15 an initial concentration of 3000 ppm to a final concentration of 500 ppm when the urea decomposition rate corresponds to an equivalent nitrogen to NO flow of 3.0.

Example 25

20 Data are obtained using a 300-foot-long, 10-foot-diameter cement kiln being fired with low sulfur western bituminous coal. The gas phase NO concentration in the exhaust prior to the application of ammonium sulfate injection is 800 ppm.

The coal fired primary zone is operated under normal conditions with 1.5% excess oxygen. Approximately 25 30 feet from the end of the kiln natural gas is added to reduce the overall stoichiometric ratio to 0.99. Approximately 15 feet from the end of the kiln at a temperature of 1000°F (540°C) ammonium sulfate is added with the final burnout air so that the overall exhaust oxygen concentration is 2.0%. The ammonium sulfate is fed at a rate sufficient to provide an equivalent nitrogen flow of 3.0 times the uncontrolled NO_x emissions.

30 Under these conditions it is found that the concentration of NO_x is reduced from initial concentrate of 600 ppm to final concentration of 180 ppm.

IV. Summary

35 In summary, it can be seen that using the two zone reaction method of introducing selective NO_x reducing agents into an effluent stream provides extremely favorable results. In particular, NO_x emissions can be reduced in excess of 80% with total NO_x emissions being below 100 ppm. The present invention has potential for use in controlling emissions from numerous types of combustion emission sources 40 including stationary boilers and the like, as well as motor vehicles.

The present invention provides that -NH and -CN containing selective reducing agents are decomposed 45 into certain decomposition products in an oxygen-free zone containing CO as the result of fuel-rich combustion processes. This zone is maintained at a temperature of from about 300°F to 3000°F (150°C to 1650°C). Once the decomposition of the selective agent is at least partially complete, the decomposition products are introduced into a second reaction zone having an excess of oxygen. The temperature within this zone is maintained at between approximately 500°F (260°C) and approximately 2800°F (1425°C).

Furthermore, it will be appreciated that SO_x control can also be combined with control of NO_x using this system. It is presently preferred to inject CaO in various forms along with cyanuric acid into the effluent stream. This results in good control of SO_x.

50 The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

55

Claims

1. A process for selectively reducing nitrogen oxides in combustion effluent streams characterized in that it comprises the steps of:
 - 5 a) introducing a reducing agent into a gaseous decomposition zone, said reducing agent having at least one functional group selected from the group comprising -NH and -CN, wherein the decomposition zone is substantially oxygen deficient and is maintained at a temperature in the range of from approximately 300°F (150°C) to approximately 3000°F (1650°C);
 - 10 b) allowing the reducing agent sufficient residence time within the decomposition zone to allow for substantial mixing of the reducing agent and gaseous species within the decomposition zone;
 - 15 c) introducing the resulting mixture from the decomposition zone to a reaction zone containing combustion effluents, said reaction zone having an excess of oxygen; and
 - 20 d) allowing the mixture from the decomposition zone sufficient residence time within the reaction zone to allow the reduction of the NO_x within the combustion effluents.
- 15 2. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claim 1 characterized in that the selective reducing agent is cyanuric acid.
- 20 3. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claims 1 or 2 characterized in that the temperature within the decomposition zone is within the range of from approximately 1400°F (760°C) and approximately 1800°F (980°C) and the temperature in the reaction zone is maintained in the range of from approximately 1200°F (650°C) to approximately 1800°F (980°C).
- 25 4. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claim 1 characterized in that the selective reducing agent is urea.
- 30 5. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claim 1 characterized in that the selective reducing agent is a compound selected from the group consisting of ammonium sulfate, ammonium carbonate, ammonium bicarbonate, ammonium formate, ammonium oxalate, ammonia, biuret, triuret, NH₂CN, Ca(CN)₂, CaCN₂, NaOCN, dicyanodiamide, and melamine.
- 35 6. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1, 4, or 5 characterized in that the temperature within the decomposition zone is within the range of from approximately 1200°F (650°C) to approximately 1900°F (1040°C) and the temperature in the reaction zone is maintained in the range of from approximately 800°F (425°C) to approximately 2400°F (1300°C).
- 40 7. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 6 characterized in that it also comprises:
 - 35 a) introducing an SO_x removal agent into the stream of combustion effluents, said combustion effluents having a temperature in the range of from approximately 800°F (425°C) to approximately 2800°F (1540°C) at the point at which the SO_x removal agent is introduced; and
 - 45 b) allowing the resulting mixture sufficient residence time to allow the reaction of SO_x with the SO_x removal agent whereby SO_x is also removed from the combustion effluent stream, said residence time being in the range of from approximately 50 milliseconds to approximately 5 seconds.
- 45 8. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claim 7 characterized in that the SO_x removal agent is selected from the group consisting of limestone, quicklime, and hydrated lime.
- 50 9. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 8 characterized in that the residence time within the decomposition zone is about 5 milliseconds to about 5 seconds and the residence time within the reaction zone is from approximately 30 milliseconds to approximately 5.0 seconds.
- 55 10. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 9 characterized in that the equivalent mole ratio of nitrogen in the reducing agent to NO_x in the combustion effluent stream is in the range of from approximately 0.5:1 to approximately 10:1.
- 55 11. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 10 characterized in that the equivalent mole ratio of nitrogen in the reducing agent to NO_x is in the range of from approximately 0.7:1 to approximately 3:1.
- 55 12. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 11 characterized in that the air to fuel stoichiometric ratio in the decomposition zone is within the range of approximately 0.7 to approximately 1.0.
- 55 13. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 12 characterized in that the fuel-rich decomposition zone is produced by using fuel injection.

14. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 13 characterized in that the excess of oxygen within the reaction zone is achieved by the injection of a gas or air containing oxygen into the decomposition zone.

15. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 14 characterized in that the reducing agent is introduced into the decomposition zone as a dry solid, as an aqueous solution, or as an alkanolic solution.

16. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 15 characterized in that the effectiveness of the reaction zone is enhanced by the addition of a radical generating promoter selected from the group consisting of hydrogen, methanol, natural gas, propane, carbon monoxide, and light petroleum fuels.

17. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 16 characterized in that the effectiveness of the reaction zone is enhanced by the use of a catalyst selected from the group consisting of stainless steel, Pt, Pd, W, Ni, Co, Au, Ag, and Mn.

18. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 17 characterized in that the SO_x removal agent is added as a dry powder.

19. A process for selectively reducing nitrogen oxides in combustion effluent streams according to any one of claims 1 to 18 characterized in that the SO_x removal agent comprises a CaO slurry.

20. A process for selectively reducing nitrogen oxides in combustion effluent streams according to claim 19 characterized in that a surfactant is added to the slurry to enhance emission reduction.

20

25

30

35

40

45

50

55

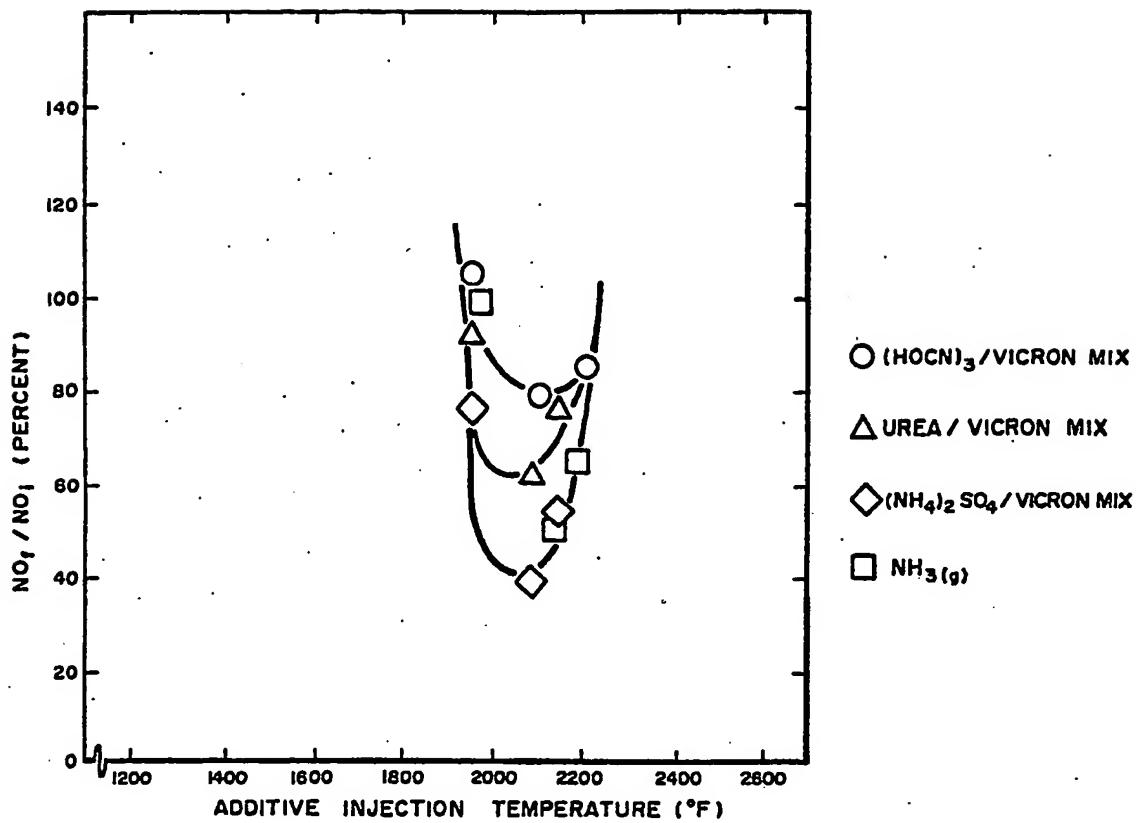


FIG. 1

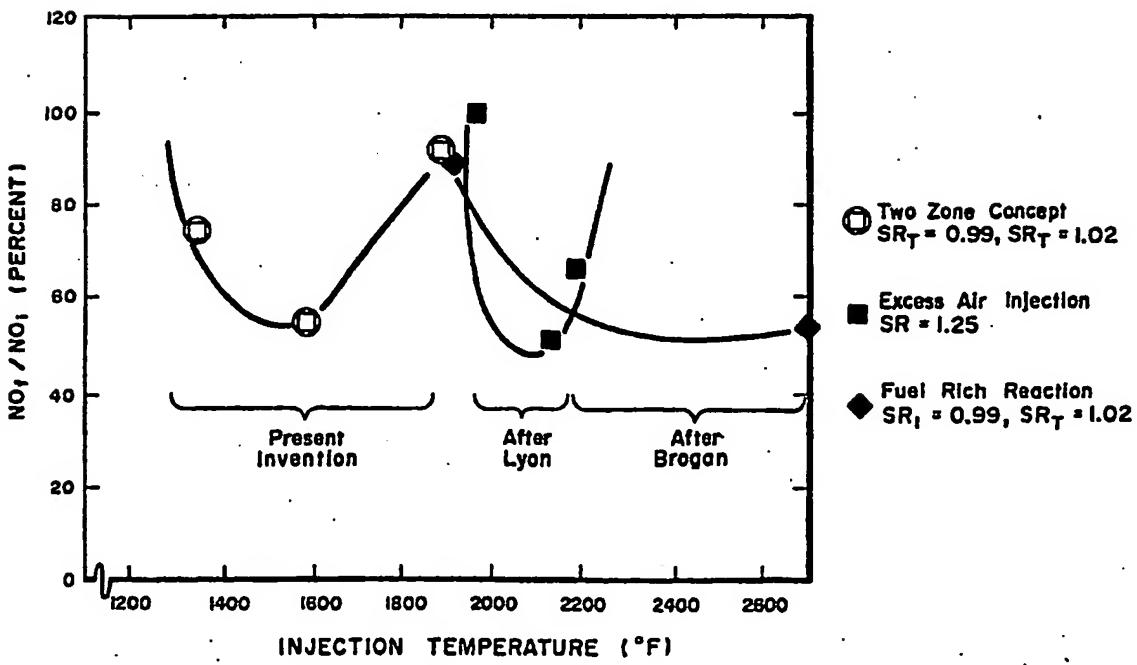


FIG. 2

BEST AVAILABLE COPY

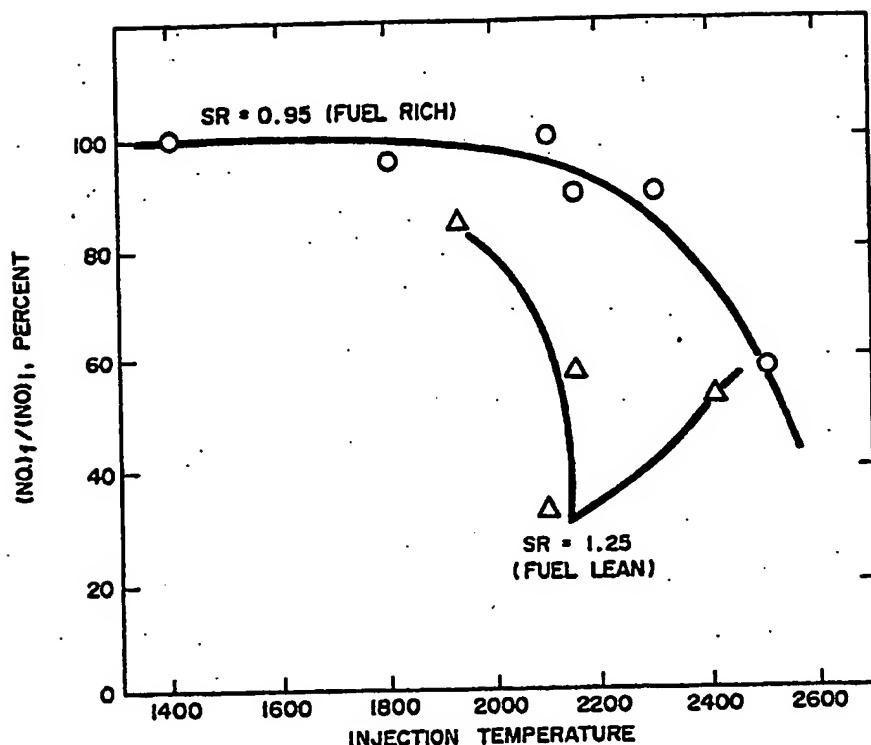


FIG. 3

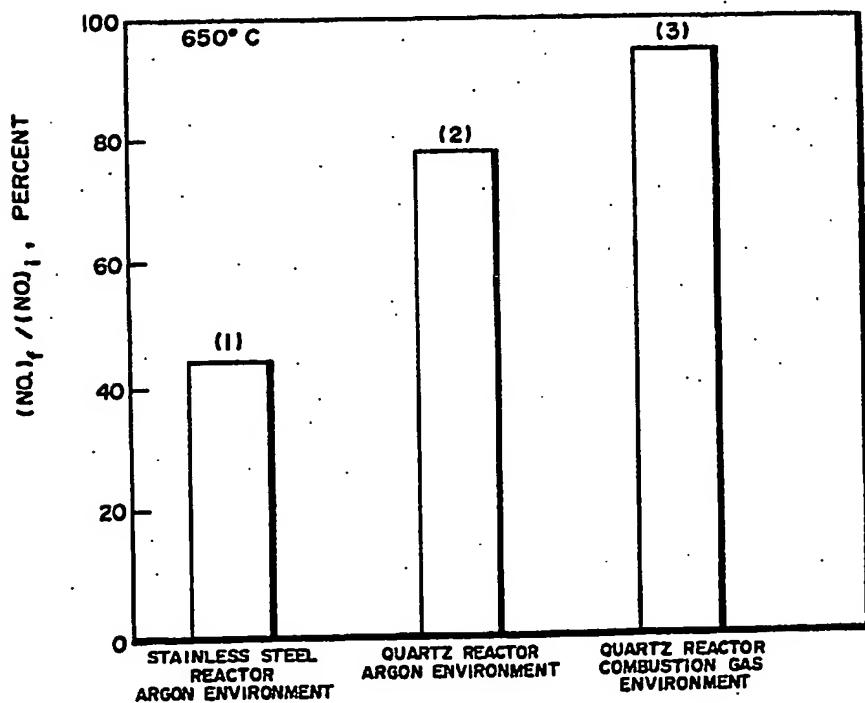


FIG. 4

BEST AVAILABLE COPY

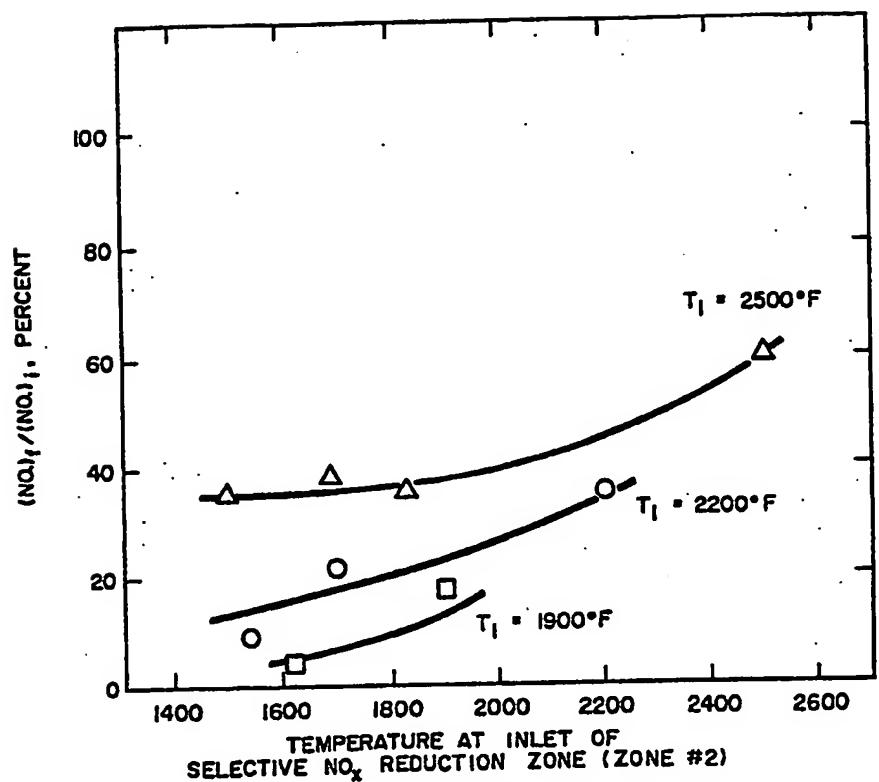


FIG. 5

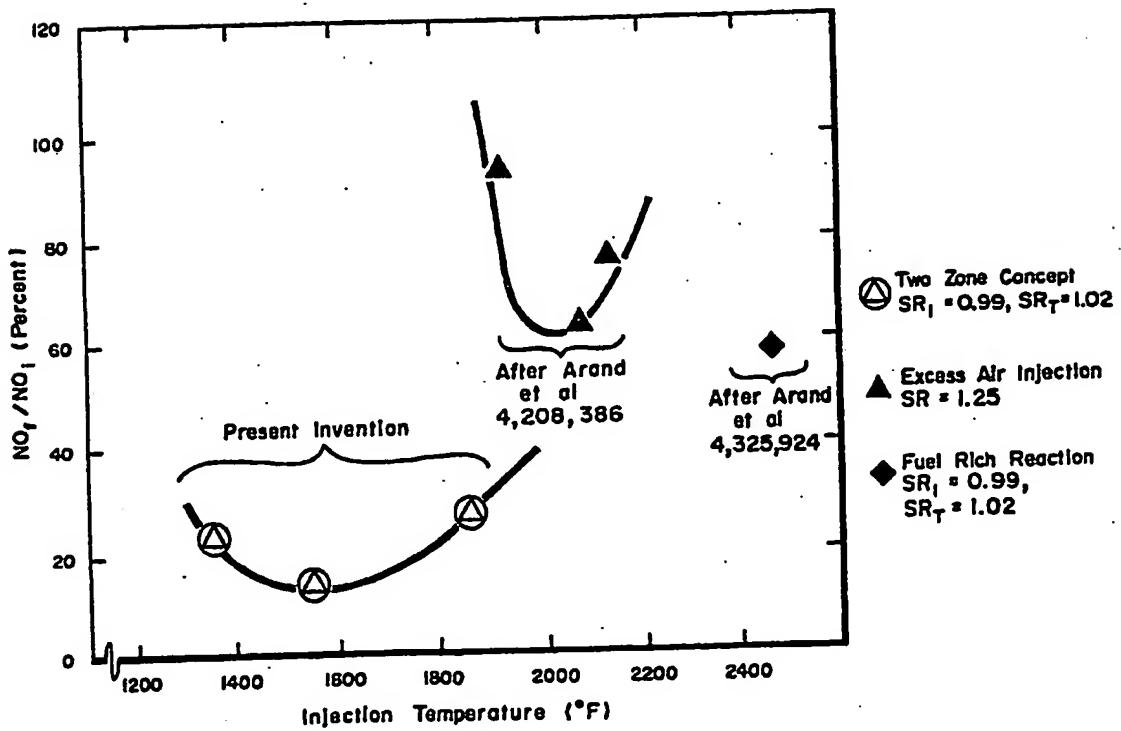


FIG. 6

BEST AVAILABLE COPY

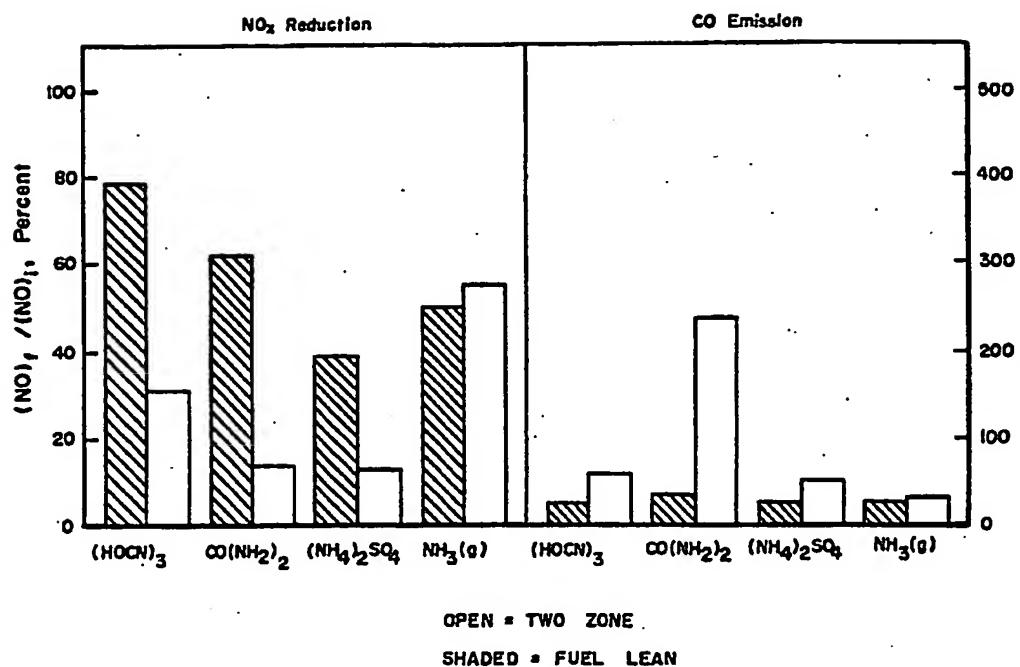


FIG. 7

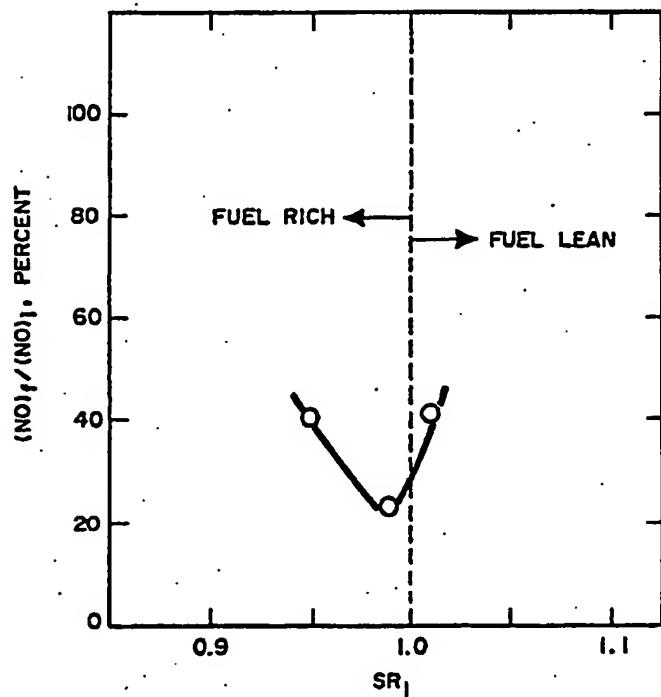


FIG. 8

BEST AVAILABLE COPY

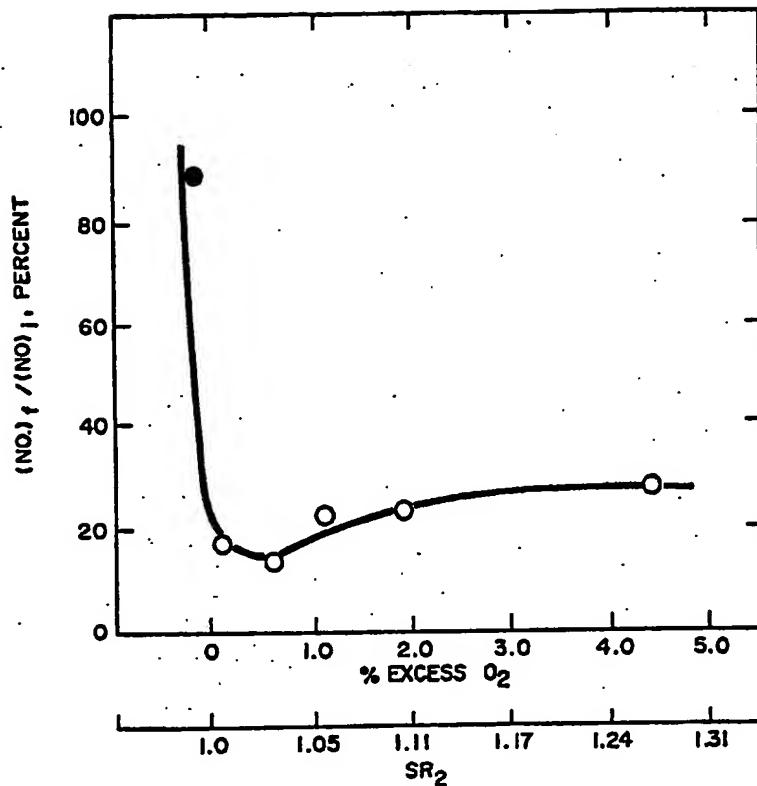


FIG. 9

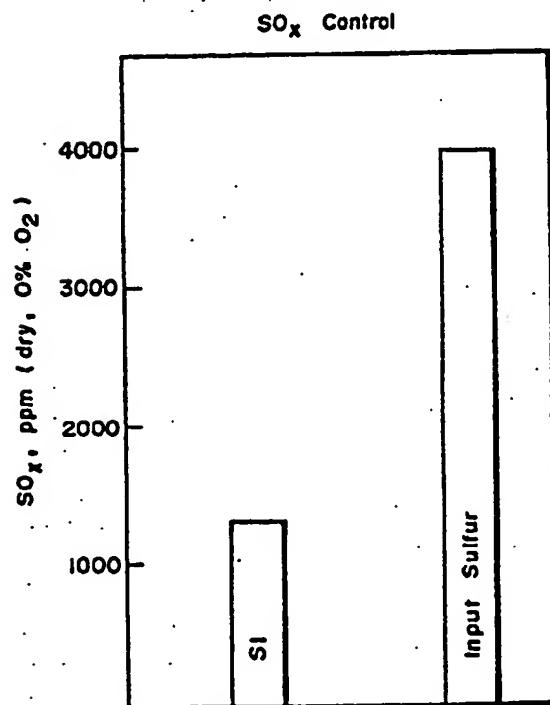


FIG. 10

BEST AVAILABLE COPY

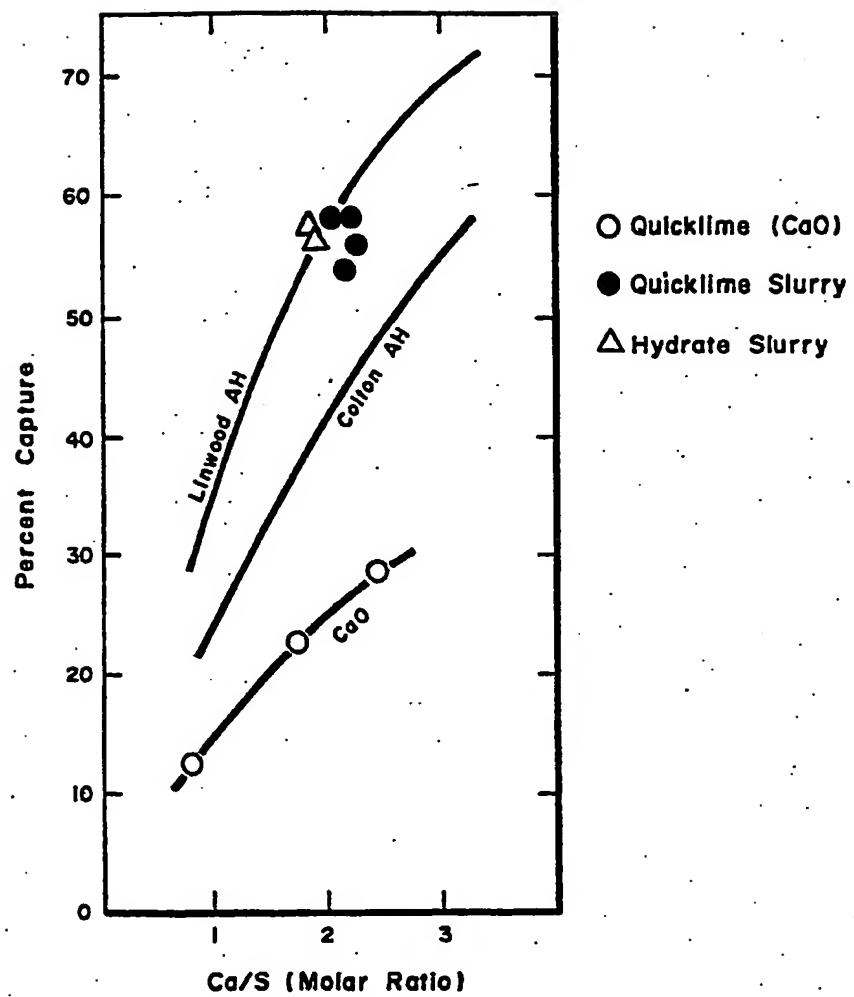


FIG. 11

BEST AVAILABLE COPY

DERWENT-ACC-NO: 1988-294601

DERWENT-WEEK: 199607

COPYRIGHT 2005 DERWENT INFORMATION LTD

TITLE: Removing nitrogen oxide(s) from combustion effluents - by addn. of reducing agents contg. nitrogenous functional groups

INVENTOR: CHEN, S L; HEAP, M P ; MCCARTHY, J M ; PERSHING, D W

PATENT-ASSIGNEE: ENERGY & ENVIRONMENTAL RES CORP[ENERN] , ENERGY ENVIRON RES[ENERN]

PRIORITY-DATA: 1987US-0073980 (July 15, 1987) , 1987US-0039324 (April 16, 1987)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	
MAIN-IPC				
EP 287224 A	October 19, 1988	E	026	N/A
DE 3854728 G	January 11, 1996	N/A	000	B01D
053/34				
US 4851201 A	July 25, 1989	N/A	015	N/A
US 4861567 A	August 29, 1989	N/A	014	N/A
EP 287224 B1	November 29, 1995	E	026	B01D
053/34				

DESIGNATED-STATES: AT BE CH DE ES FR GB GR IT LI LU NL AT BE CH DE ES FR GB GR IT LI LU NL SE

CITED-DOCUMENTS: A3...199050; DE 3447616 ; GB 1488087 ; No-SR.Pub ; US 4335084 ; WO 8706923

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
EP 287224A	N/A	1988EP-0302535	March 23, 1988
DE 3854728G	N/A	1988DE-3854728	March 23, 1988
DE 3854728G	N/A	1988EP-0302535	March 23, 1988
DE 3854728G	Based on	EP 287224	N/A
US 4851201A	N/A	1987US-0073980	July 15, 1987
US 4861567A	N/A	1987US-0039324	April 16, 1987
EP 287224B1	N/A	1988EP-0302535	March 23, 1988

INT-CL (IPC): B01D053/34, B01J008/00 , C01B017/00 , C01B021/00

ABSTRACTED-PUB-NO: EP 287224A

BASIC-ABSTRACT:

(i) A redn. agent contg. -NH and/or -CN groups is introduced into an O₂ deficient decomposition zone at 150-1650 deg.C. (ii) Decomposition prod. obtnd. is fed to a reaction zone contg. excess O₂ and mixed with effluent to effect redn. of its nitrogen oxides content at 250-1425 deg.C. If the effluent further contains sulphur oxides then e.g. limestone, quick lime etc. is opt. added to effect their removal. Pref. reagent in (i) is urea, cyanuric acid, Ca(CN)₂, NH₃ etc. and may be added as solids, aq. solns. etc. Pref. a radical

generating promoter e.g. H₂, MeOH, CO etc. plus a catalyst e.g. Pt, Pd, W etc. are added in (ii).

USE/ADVANTAGE - Effluent source is e.g. automobile engines, incinerators, furnaces, turbines. Process is low cost and nitrogen oxide levels can be reduced to below 100 ppm. leading to lower atmos. pollution. Sulphur oxides can be removed simultaneously.

ABSTRACTED-PUB-NO: EP 287224B

EQUIVALENT-ABSTRACTS:

A process for selectively reducing nitrogen oxides in a gaseous combustion effluent stream comprising introducing a nitrogen-containing reducing agent into a first oxygen-deficient and fuel-rich zone and introducing the resulting mixture into a second fuel-lean zone having an excess of oxygen, characterised in that it comprises the steps of a) introducing a reducing agent having at least one functional group selected from the group comprising -NH and -CN into a first gaseous decomposition zone being fuel-rich and oxygen deficient or oxygen free and being maintained at a temperature in the range of from 1200 deg F (650 deg C) to 1900 deg F (1040 deg C) b) allowing the reducing agent sufficient residence time within the decomposition zone to allow for its decomposition and for the mixing of the gaseous species within the decomposition zone; c) introducing the resulting mixture from the decomposition zone to a second fuel -lean reaction zone having an excess of oxygen and through which the combustion effluent stream is being directed, the temperature in the reaction zone being maintained in the range of from 800 deg (425 deg.C) to 2400 deg (1300 deg.C); and d) allowing the mixture from the decomposition zone sufficient residence time within the reaction zone to allow the reduction of the NO_x within the combustion effluent.

US 4851201A

Nitrogen oxides in combustion effluent streams are selectively reduced by (a) introducing a reducing agent into a gaseous decompsn. zone contg. no O₂, which is maintained at 300-2400 deg.F, (b) introducing mixt. obtd. into a reaction zone contg. excess O₂ and combustion effluents, and (c) allowing a residence time so that nitrogen oxides within effluents are reduced. Reducing agents contg. NH and/or CN as functional gps., and pref. comprises urea, (NH₄)₂SO₄, NH₄HCO₃, HCOONH₄, NH₃, NH₂CN, Ca(CN)₂, CaCN₂, NaOCN, ammonium oxalate, biuret, triuret, dicyanodiamide or melamine. ADVANTAGE - Can be used in conjunction with a system for simultaneous nitrogen oxides and sulphur oxides control.

(15pp)

US 4861567A

Nitrogen oxides in combustion effluent streams are selectively reduced by (a) introducing cyanuric acid into a gaseous decomposition zone deficient in O₂ but contg. CO and H₂O, and maintained at 1000-3000 deg. F; and (b) allowing cyanuric acid to reside there for a time to allow mixing with gaseous species. Process then comprises (c) introducing mixt. obtd. to a reaction zone contg. excess O₂ and combustion effluents; and (d) allowing it to reside there for a time to achieve redn. of nitrogen oxides. ADVANTAGE - Can be combined with sulphur oxide control technology.

(14pp)

CHOSEN-DRAWING: Dwg.0/11 Dwg.0/11

TITLE-TERMS: REMOVE NITROGEN OXIDE COMBUST EFFLUENT ADD REDUCE AGENT CONTAIN
NITROGENOUS FUNCTION GROUP

DERWENT-CLASS: E36 J01

CPI-CODES: E31-F01A; E31-H01; E31-H02; E34-D01; E34-D03; J01-E02; J01-E02D;
N02-F; N03-C;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

Fragmentation Code

C107 C108 C216 C307 C316 C520 C540 C730 C800 C801
C802 C803 C804 C805 C807 M411 M750 M903 M904 M910
N163 N515 Q431 Q436 Q439

Specfic Compounds

01784X 01953X

Registry Numbers

3102R 1678D

Chemical Indexing M3 *02*

Fragmentation Code

J0 J011 J1 J171 M280 M320 M416 M620 M630 M781
M903 M904 M910 N163 Q431 Q436 Q439 Q508 Q509

Specfic Compounds

07340R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *03*

Fragmentation Code

C101 C106 C108 C316 C500 C530 C540 C730 C800 C801
C802 C804 C806 C807 M411 M781 M903 M904 N163 Q431
Q436 Q439 Q508 Q509

Specfic Compounds

01304R 01786R 05417R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *04*

Fragmentation Code

J0 J012 J1 J172 K0 L5 L560 M280 M320 M416
M620 M630 M781 M903 M904 M910 N163 Q431 Q436 Q439
Q508 Q509

Specfic Compounds

03138R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *05*

Fragmentation Code

K0 L4 L432 M280 M320 M416 M620 M781 M903 M904
M910 N163 Q431 Q436 Q439 Q508 Q509

Specfic Compounds

00123R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *06*

Fragmentation Code

F012 F014 F016 F580 H1 H101 H123 L9 L910 L999

M280 M320 M413 M510 M521 M530 M540 M781 M903 M904
M910 N163 Q431 Q436 Q439 Q508 Q509

Ring Index

00212

Specfic Compounds

00859R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *07*

Fragmentation Code

F012 F014 F016 F580 J5 J523 L9 L910 L999 M280
M320 M413 M510 M521 M530 M540 M781 M903 M904 M910
N163 Q431 Q436 Q439 Q508 Q509

Ring Index

00212

Specfic Compounds

00860R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *08*

Fragmentation Code

K0 L4 L431 L499 M280 M320 M416 M620 M781 M903
M904 N163 Q431 Q436 Q439 Q508 Q509

Specfic Compounds

00838R 14762R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *09*

Fragmentation Code

C101 C106 C107 C520 C730 C800 C801 C802 C806 C807
M411 M781 M903 M904 M910 N163 Q431 Q436 Q439 Q508
Q509

Specfic Compounds

01248R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *10*

Fragmentation Code

A111 A220 A940 C106 C107 C108 C520 C730 C801 C802
C803 C806 C807 M411 M781 M903 M904 N163 Q431 Q436
Q439 Q508 Q509

Specfic Compounds

07979R 10663R 14763R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *11*

Fragmentation Code

K0 L1 L110 L2 L250 M280 M320 M416 M620 M781
M903 M904 M910 N163 Q431 Q436 Q439 Q508 Q509

Specfic Compounds

01264R

Registry Numbers

3102R 1678D

Chemical Indexing M3 *12*

Fragmentation Code
A425 A426 A427 A428 A546 A547 A674 A678 A679 C810
M411 M730 M903 Q421
Registry Numbers
3102R 1678D

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0123U; 0246U ; 0838U ; 0859U ; 0860U ; 1152U
; 1248U ; 1264U ; 1304U ; 1784U ; 1786U ; 1953U

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1988-130530